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# Hydrogen bonding in 2-(hydroxymethyl)-1,3-propanediol and *N*,*N*′-bis[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]malonamide

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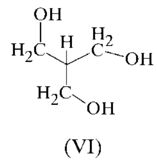
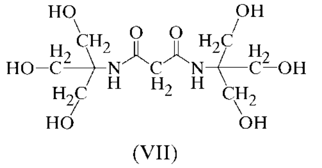
The molecule of 2-(hydroxymethyl)-1,3-propanediol, $C_4H_{10}O_3$, lies across a mirror plane in space group $P2_1/m$, with disorder of both terminal hydroxyl H atoms. The molecules are linked by three O—H···O hydrogen bonds which combine to form sheets; in each O—H···O bond, the H atom resonates between the two O atoms. In the crystal structure of *N*,*N*′-bis[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]malonamide, $C_{11}H_{22}N_2O_8$, the molecule lies about a twofold axis and has four strong hydrogen bonds which form a mixture of chains and dimers; these combine to give a three-dimensional supramolecular framework.

## Comment

The supramolecular structure of *N*,*N*′-bis[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]ethanediamide, $(HOCH_2)_3CNHCOCONHC(CH_2OH)_3$, (I), was recently reported to be two-dimensional, despite the presence of six independent hydrogen bonds (Ross *et al.*, 2001). The aminotriol parent of (I), namely $H_2NC(CH_2OH)_3$, (II) (Eilerman & Rudman, 1980; Castellari & Ottani, 1997), also has a two-dimensional supramolecular structure in the orthorhombic phase, as does pentaerythritol, $C(CH_2OH)_4$, (III) (Ladd, 1979; Eilerman & Rudman, 1979*a*; Hope & Nichols, 1981; Semmingsen, 1988; Katrusiak, 1995; Batten & Robson, 1998). In contrast, the hydrogen-bonding arrangements in 3-hydroxy-2,2-bis(hydroxymethyl)propanoic acid, $HO_2CC(CH_2OH)_3$, (IV) (Eilerman & Rudman, 1979*b*), and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, $CH_3CH_2C(CH_2OH)_3$, (V) (Zakaria *et al.*, 2001), produce a three-dimensional array. The supramolecular structures of 2-(hydroxymethyl)-1,3-propanediol, (VI), and *N*,*N*′-bis-[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]-malonamide, (VII), have now been determined and compared to those of compounds (I)–(V).



(VI)



(VII)

A general view of the molecule of (VI) is shown in Fig. 1. Atoms C1, C2 and O1 lie on the mirror plane, leading to disorder of the hydroxyl H atom bonded to atom O1. Similarly, there is disorder of the second hydroxyl group, resulting in three strong hydrogen bonds (Table 1). In fact, it can be considered that the H atoms resonate between the O atoms, so that a continous network of hydrogen bonds forms. In Fig. 2, H atoms have been omitted to make this network clearer; the dashed lines represent O—H···O bonds where the H atom may be coordinated to either O atom. Two chains form: (i) from O2—H2*C*···O1($1-x$, $y-\frac{1}{2}$, $1-z$), leading to a *C*(8) chain along (010), which combine to form a series of $R_2^2(12)$ rings (Fig. 2); (ii) from a combination of the first hydrogen bond and O2—H2*B*···O2($-x$, $-y$, $-z$), resulting in *C*(8)

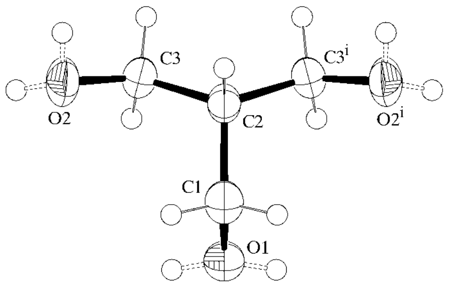


**Figure 1**
A view of the molecule of (VI), showing the atom-numbering scheme. The molecule lies across the mirror [symmetry code: (i) $x$, $-y+\frac{1}{2}$, $z$]. Dashed lines indicate disorder of the terminal H atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.

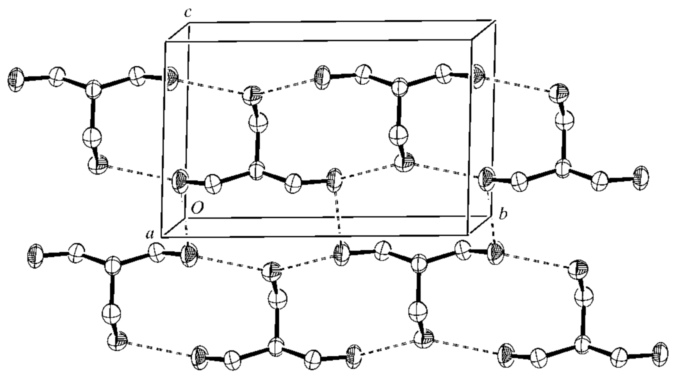


**Figure 2**
The arrangement of molecules of (VI) within the unit cell, showing the formation of sheets normal to [100]. Dashed lines indicate O—H···O bonds in which H atoms resonate between the two O atoms, as indicated by the disorder, shown as in Fig. 1.

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chains and $R_4^4(12)$ rings, which combine to form a sheet, shown normal to [100] in Fig. 2.

A sheet arrangement of molecules was also found for the trihydroxy compound, (V) (Zakaria *et al.*, 2001). The framework in (V) consists of parallel molecular ladders, generated by two of the three O—H···O hydrogen bonds. The ladders are linked together by the third hydrogen bond (Zakaria *et al.*, 2001). In the tetrahydroxy compound, (III), the two-dimensional (sheet) structure is created by each molecule linking to four others through O—H···O hydrogen bonds; all the hydroxyl groups in (III) act as hydrogen-bond acceptors and donors (Ladd, 1979; Eilerman & Rudman, 1979*a*; Hope & Nichols, 1981; Semmingsen, 1988; Katrusiak, 1995; Batten & Robson, 1998).

*N,N′*-Bis-2-hydroxy-1,1-bis(hydroxymethyl)ethyl]malonamide, (VII) (Fig. 3), crystallizes in space group *C*2/*c* with atom C6 on a twofold axis.

Four strong hydrogen bonds form (Table 2); amide atom N1 donates to hydroxyl atom O3 [N1—H1···O3($x$, $y + 1$, $z$)], to form a *C*(5) chain along [010]. The symmetry of the molecule leads to two parallel *C*(5) chains, giving linked $R_2^2(18)$ rings

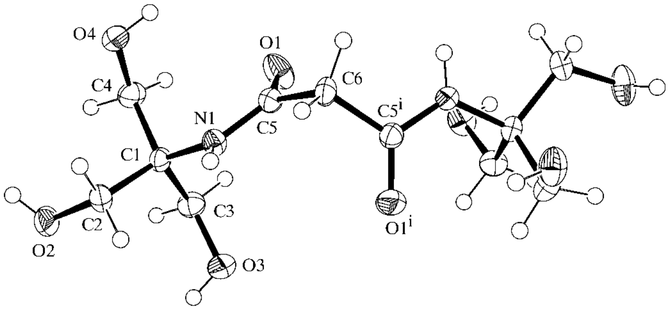

**Figure 3**
A view of the molecule of (VII), showing the atom-numbering scheme and the formation of the molecule *via* a symmetry operation [symmetry code: (i) $-x$, $y$, $-z + \frac{1}{2}$]. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.

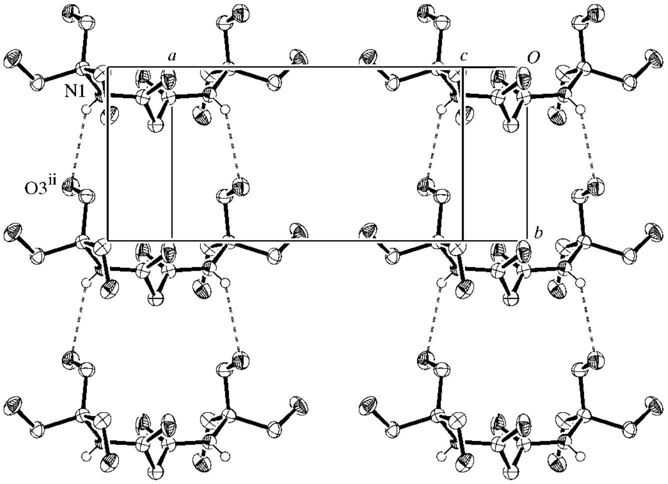

**Figure 4**
Part of the crystal structure of (VII), showing the *C*(5) chains formed from N1—H1···O3$^{ii}$ hydrogen bonds [symmetry code: (ii) $x$, $y + 1$, $z$].

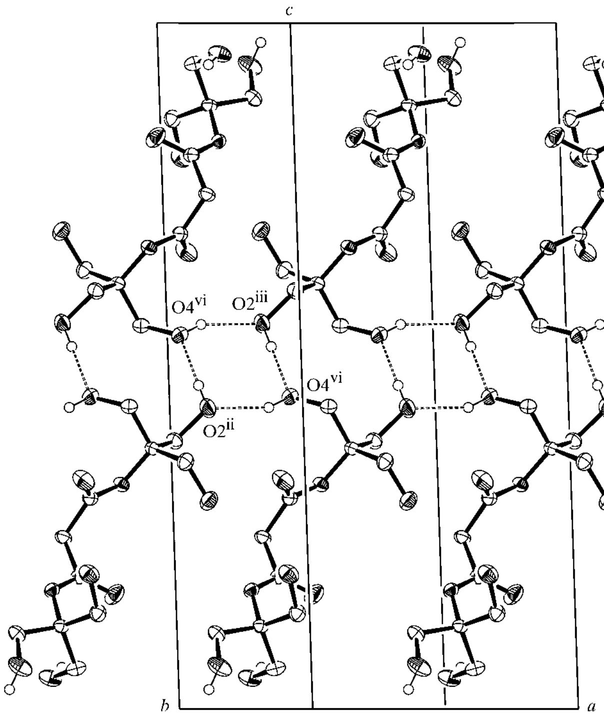

**Figure 5**
Part of the crystal structure of (VII), showing the sheets formed from two hydrogen bonds [O2—H2···O4$^{iv}$ and O4—H4···O2$^{iii}$; symmetry codes: (iii) $-\frac{1}{2} + x, \frac{1}{2} + y, z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$], resulting in an $R_4^4(8)$ ring, *viz.* O4—H4···O2$^{ii}$—H2$^{ii}$···O4$^{vi}$—H4$^{vi}$···O2$^{iii}$—H2$^{iii}$···O4 [symmetry codes: (ii) $x, y + 1, z$; (vi) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$].

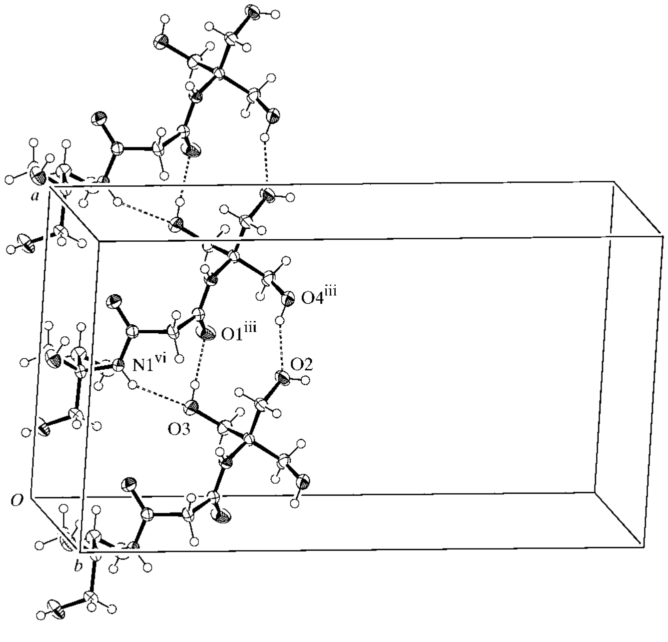

**Figure 6**
The combination of three hydrogen bonds in the structure of (VII), *i.e.* N1—H1···O3, O3—H3···O1 and O4—H4···O2. This gives *C*(5), *C*(7) and *C*(13) chains which combine to give $R_2^2(8)$ and $R_2^2(13)$ rings. [Symmetry codes: (iii) $-\frac{1}{2} + x, \frac{1}{2} + y, z$; (vi) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

(Fig. 4). The hydroxyl atoms O2 and O4 act as both donor and acceptor; O4—H4···O2($-\frac{1}{2} + x, \frac{1}{2} + y, z$) leads to a $C(13)$ chain along [$\bar{1}10$], whilst O2—H2···O4($\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$) gives rise to a dimer centred on the inversion at ($\frac{1}{4},\frac{1}{4},\frac{1}{2}$), leading to an $R_2^2(12)$ motif. The two combine to give a sheet containing adjacent $R_4^4(8)$ and $R_2^2(12)$ rings, O2—H2···O4—H4···O2 (Fig. 5). The final hydrogen bond again has a hydroxyl O atom as donor, but with the C=O group as acceptor, O3—H3···O1($\frac{1}{2} + x, -\frac{1}{2} + y, z$), thus generating a $C(7)$ chain along [$1\bar{1}0$]. The four hydrogen bonds combine in a number of ways. In addition to the formation of the $R_4^4(8)$ ring shown in Fig. 5, $C(5)$ and $C(7)$ combine to form an $R_2^2(8)$ ring, whilst $C(7)$ and $C(13)$ combine to give an $R_2^2(13)$ motif; both of these are shown in Fig. 6. Finally, all hydrogen bonds combine *via* the linking dimer to form a three-dimensional framework (Fig. 7).

The additional methylene group in (VII) results in significant structural differences between (I) (Ross *et al.*, 2001) and (VII), the most striking being the change from a two-dimensional supramolecular network in (I) to the three-dimensional arrangement in (VII). The amido NH units in (I) take no part in the supramolecular aggregation, being solely involved in intramolecular hydrogen bonding with the adjacent carbonyl O atoms (Ross *et al.*, 2001). Each molecule of (I) acts as a fourfold donor and acceptor in intermolecular hydrogen bonding and each molecule of (I) is thereby linked to six others in the resulting two-dimensional array (Ross *et al.*, 2001). In the aminotriol (II), the amino group is involved in the intermolecular hydrogen bonding. However, despite there being four distinct hydrogen bonds (two O—H···O, one O—H···N and one N—H···O), the supramolecular structure is only two-dimensional (Eilerman & Rudman, 1980; Castellari & Ottani, 1997).

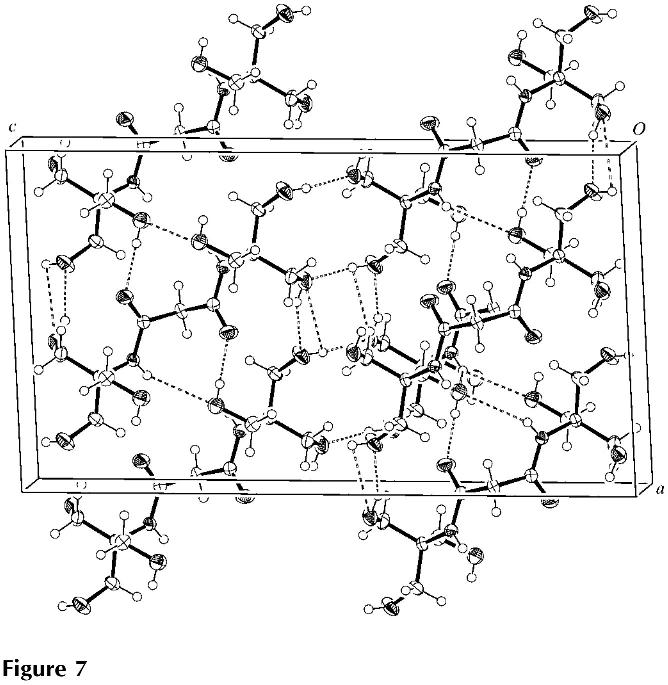

**Figure 7**
The unit cell of (VII), showing the formation of a three-dimensional framework of hydrogen bonds.

## Experimental

Compound (VI) was a commercial sample and was recrystallized from dry ethyl acetate. Compound (VII) was prepared from (II) (0.045 mol) and diethyl malonate (0.023 mol) in refluxing methanol for 2 h. On cooling, colourless crystals of (VII) slowly formed. The product was recrystallized from aqueous EtOH (yield 90%, m.p. 428 K). $^1$H NMR (Me$_2$SO-$d_6$, p.p.m.): $\delta$ 3.15 (*s*, 2H, COCH$_2$), 3.539 (*d*, 12H, CH$_2$OH), 4.63 (*t*, 6H, OH), 7.55 (*s*, 2H, NH). $^{13}$C NMR (Me$_2$SO-$d_6$, p.p.m.): $\delta$ 44.4 (COCH$_2$), 60.6 (CH$_2$OH), 62.9 (C-quarternary), 168.8 (CO). IR (KBr): $\nu$ 3361 and 3308 (OH), 3217 (NH), 2970, 2953 and 2883 (CH), 1648 (CO).

### Compound (VI)

*Crystal data*

$C_4H_{10}O_3$
$M_r = 106.12$
Monoclinic, $P2_1/m$
$a = 4.8066$ (3) Å
$b = 9.5179$ (6) Å
$c = 6.1346$ (4) Å
$\beta = 107.911$ (4)°
$V = 267.05$ (3) Å$^3$
$Z = 2$

$D_x = 1.320$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 1123 reflections
$\theta = 2.9$–27.5°
$\mu = 0.11$ mm$^{-1}$
$T = 292$ (2) K
Prism, colourless
0.26 × 0.12 × 0.05 mm

*Data collection*

Enraf–Nonius KappaCCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: empirical (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.949$, $T_{\max} = 0.994$
2166 measured reflections

629 independent reflections
504 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 27.4°$
$h = -5 \rightarrow 6$
$k = -12 \rightarrow 11$
$l = -7 \rightarrow 7$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.103$
$S = 1.04$
629 reflections
46 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 0.0278P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.17$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.16$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.21 (5)

**Table 1**
Hydrogen-bonding geometry (Å, °) for (VI).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···O2$^{\rm i}$ | 0.82 | 1.91 | 2.7130 (11) | 167 |
| O2—H2*B*···O2$^{\rm ii}$ | 0.82 (4) | 1.91 (4) | 2.729 (2) | 173 (4) |
| O2—H2*C*···O1$^{\rm iii}$ | 0.79 (4) | 1.93 (4) | 2.7130 (11) | 175 (4) |

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $-x, -y, -z$; (iii) $1 - x, y - \frac{1}{2}, 1 - z$.

### Compound (VII)

*Crystal data*

$C_{11}H_{22}N_2O_8$
$M_r = 310.31$
Monoclinic, $C2/c$
$a = 11.6928$ (11) Å
$b = 5.6610$ (5) Å
$c = 21.0034$ (19) Å
$\beta = 92.700$ (2)°
$V = 1388.7$ (2) Å$^3$
$Z = 4$

$D_x = 1.484$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3982 reflections
$\theta = 3.7$–32.3°
$\mu = 0.13$ mm$^{-1}$
$T = 292$ (2) K
Plate, colourless
0.50 × 0.50 × 0.10 mm

**Table 2**
Hydrogen-bonding geometry (Å, °) for (VII).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N1—H1$\cdots$O3$^{i}$ | 0.86 | 2.58 | 3.2445 (16) | 135 |
| O4—H4$\cdots$O2$^{ii}$ | 0.82 | 2.03 | 2.8037 (16) | 157 |
| O2—H2$\cdots$O4$^{iii}$ | 0.82 | 1.91 | 2.7238 (15) | 172 |
| O3—H3$\cdots$O1$^{iv}$ | 0.82 | 1.89 | 2.7069 (16) | 175 |
| C4—H4$A\cdots$O1 | 0.97 | 2.47 | 2.9227 (19) | 108 |

Symmetry codes: (i) $x, 1+y, z$; (ii) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (iv) $\frac{1}{2}+x, y-\frac{1}{2}, z$.

*Data collection*

Bruker SMART 1000 CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.869$, $T_{\max} = 0.987$
6754 measured reflections
2473 independent reflections
2027 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\max} = 32.5°$
$h = -10 \rightarrow 17$
$k = -8 \rightarrow 8$
$l = -31 \rightarrow 31$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.187$
$S = 1.06$
2473 reflections
103 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1186P)^2 + 0.6984P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.46$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.27$ e Å$^{-3}$

All H atoms were placed in geometrically calculated positions and refined using a riding model. *PLATON* (Spek, 2002) was used for the analysis of the hydrogen bonding.

For compound (VI), data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*. For compound (VII), data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*. For both compounds, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* in *OSCAIL* (McArdle, 1994, 2000) and *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1567). Services for accessing these data are described at the back of the journal.

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